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USSR Report

CHEMISTRY

No. 77

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USSR REPORT

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ORGANOPHOSPHORUS COMPOUNDS

UDC 543.544.2:547.94

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Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 4, Jul-Aug 81 (manuscript received 1 Apr 81) pp 33-43

GLADYSHEV, P.P., GORYAYEV, M.I., BEKTENOVA, G.A., MATANTSEVA, Ye.F. and KAMENSKIY, N.P., Institute of Chemical Sciences, Kazakh SSR Academy of Sciences, Alma-Ata

[Abstract] A mathematical analysis was performed on the various factors (pH, buffer concentration, alkaloid pK_a, ionic strength, flow rate, etc.) affecting the efficiency of ion exchange chromatography of several alkaloids (morphine, codeine, noscapine, papaverine, etc.) on modified P-cellulose columns. The resultant data defined conditions for optimum analytical resolution of the alkaloids in question using different commercial cellulose products; a table could be created of the association constants for the alkaloids tested. Figures 6; references 14: 5 Western, 9 Russian.
[145-12172]

UDC 543.24+543.80

POTENTIOMETRIC TITRATION OF O,O-DIARYLPHOSPHORIC ACID HYDRAZIDES WITH SODIUM NITRITE

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNOLOGIYA in Russian Vol 24, No 7, Jul 81 (manuscript received 17 Dec 79) pp 834-836

YANCHUK, N. I., Chair of Organic Chemistry, Ternopol' State Pedagogical Institute imeni Ya. A. Galan

[Abstract] A potentiometric method for the analysis of O,O-diarylphosphoric acid hydrazides was devised, based on their reaction with sodium nitrite in hydrochloric acid leading to the formation of the corresponding azides. Optimum results are obtained in 0.01-0.04 N HCl at 25°C. An actual operation consisted of the addition of 25-35 mg of the hydrazide to a 100 ml flask containing 20 ml benzene, followed by the addition of 10 ml of 0.03 N HCl and 0.1 g potassium bromide. The electrode was then inserted and, with mixing, aliquots of 0.01 N sodium nitrite were added with readings taken after every addition. The accuracy of the method was better than 0.4%. References 8: 1 Polish, 7 Russian.
[144-12172]

UDC 543.8

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Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 36, No 8, Aug 81 (manuscript received 1 Jul 80) pp 1600-1604

BYSTRYAKOV, V. P., OBTEMPERANSKAYA, S. I, and BUKHTENKO, L. N., Moscow State University imeni M. V. Lomonosov

[Abstract] Spectrophotometric studies were carried out on the reactions of seven secondary and tertiary phosphine sulfides (in dichloroethane, chloroform,

etc.) with tetracyanethylene (in acetonitrile) to determine the feasibility of photometric analysis of the resultant charge-transfer complexes. Spectral analysis showed that reaction of the sulfides with tetracyanethylene under the conditions employed led to the appearance of orange-colored 1:1 charge-transfer complexes with absorption maxima in the 447-461 nm range. A bathochromic shift of the charge transfer band was seen when the primary ionization potential of the sulfide decreased, or when the polarity of the chlorine-based solvent was increased. Increasing the polarity of the solvent led to a decrease in the molar extinction coefficient. The method is capable of detecting phosphine sulfides in the 5×10^{-4} to 10^{-2} mole/liter range with a standard deviation of less than 0.02. References 24: 9 Russian, 14 Western.
[157-12172]

UDC 543.544

MICROANALYSIS OF ARSENATE AND PHOSPHATE IONS BY PEAK PAPER CHROMATOGRAPHY

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 36, No 8, Aug 81 (manuscript received 8 Jul 80) pp 1657-1659

BARDIN, V. V., MOKHOV, A. A. and SHICHKO, V. A., Leningrad Technological Institute imeni Lensovet [Leningrad Soviet]

[Abstract] Two techniques are described for paper chromatographic analysis of phosphate and arsenate ions, involving chromatography on FN-3 paper impregnated with $Pb(NO_3)$ and development with KI to yield white peaks against a yellow background. Recovery studies showed that best results were obtained at pH 7 with PO_4^{3-} and AsO_4^{3-} applied in amounts ranging from 4 to 20 mcg, with the standard deviation being less than 1.8 for phosphate ions and 1.5 for arsenate. References 4 (Russian).
[157-12172]

CHEMICAL INDUSTRY

AWAITING COMPLETION

Kiev POD ZNAMENEM LENINIZMA in Russian No 8, Apr 80 pp 52-55

[Article by O. Avilov, division head, chemical industry, Central Committee of the Ukrainian Communist Party]

[Text] A special role belongs to the chemical sectors of industry in accelerating the technical progress and enhancing the efficiency of the state of the art of public production. Chemistry has long been a powerful force: it has enriched man's life with a tremendous amount of synthetic materials having properties which are not found in natural materials.

Because of the continuing concern of the communist party, domestic chemical industry has been virtually reborn during the era of Soviet authority and in a relatively short time has turned into a major sector of heavy industry. Various kinds of fuel, automotive tires, mineral fertilizers, plastics, chemical fibers and synthetic dyes, magnetic tapes and movie film--this enumerates but a small portion of the over 50,000 items produced by the chemical industry in our country which have found their wide application in industry, agriculture, transportation, health care and culture.

Nowadays it would be impossible for us to imagine our lives and lifestyle without modern synthetic materials.

Within the 9th Five-Year Plan and the four years of the 10th Five-Year Plan, the volume of production in chemical sectors has almost doubled. There has been a large cut between the levels of chemical product output in the USSR and USA. The Soviet Union is in leading position in the volume of production of chemical products in Europe and in second place in the world.

Particularly great success has been achieved by our chemists in increasing the capacities of fertilizer production. In 1975, as envisaged by directives of the 24th Congress of the CPSU, 90,000 tons of fertilizer were produced. We were thus able to surpass the USA not only in rates, but in volume of production of fertilizer as well and take over the world lead. In 1977, in fact, the USSR produced twice as much of this important chemical product as the Federal Republic of Germany, England, Italy and France together.

The Soviet Union holds the world lead in petroleum processing, production of sulfuric acid, calcined soda, ammonia, chemical fiber and other kinds of products.

The working classes of the Ukraine have contributed greatly to tackling the problem of chemization of the national economy. The republic now produces more than 20 percent of the fertilizer, ammonia, sulfuric acid and calcined soda made in the country; more than a third of the synthetic dyes, almost a half of the movie film and magnetic tapes, about 80 percent of the natural sulfur and many other chemical products.

As envisaged by the targets of the 10th Five-Year Plan, the chemical sectors are continuing to develop at a record-breaking pace. Enterprise personnel under the leadership of party organizations have achieved positive results in implementing the historic decisions of the 25th Congress of the CPSU and 25th Congress of the Ukrainian Communist Party.

On 21 Dec 79, workers in the petroleum processing and petrochemical industry completed the four-year schedule of the five-year plan ahead of time in production volume. Hundreds and thousands of tons of high-octane gasoline, fuel oil, tens of thousands of automotive tires were produced, coming to 27,000,000 rubles of consumer goods. The average annual increase in production in these sectors was 11 percent: production of diesel fuel was 1.6 times as great; fuel oil was 1.8 times as great; petroleum processing was 1.7 times as great. By reconstruction and intensification of technological processes at existing facilities alone, the increase in petroleum refining amounted to several million tons, and tire production came to tens of thousands of pieces per year.

At the July, 1978 Plenum of the Central Committee of the CPSU, a program was elaborated for future development of agriculture with the aim of providing reliable consumer goods for the people and raw materials for industry. "Among the steps to intensify agricultural production," stated comrade L. I. Brezhnev, secretary of the Central Committee of the CPSU, chairman of the Presidium of the USSR Supreme Soviet, "future development of production of mineral fertilizers and means of plant protection merit the most serious attention. Without this it would today be impossible to lead agricultural production along the road to rapid enhancement".

In the four years of the five-year plan, the republic has constructed and put into operation several large plants to produce mineral fertilizers having a total capacity of more than 3,400,000 tons per annum, including 990,000 tons of carbamide in Gorlovka, 660,000 tons of liquid fertilizer complexes each in Rovno, Sumy and Cherkassy. Is that a little or a lot? A comparison will help answer that question. In the prewar Ukraine of 1940, all capacities for fertilizer manufacture were one third as great as this increase.

In the 9th Five-Year Plan, the Lisichanskiy petroleum refining plant and Odessa portside facility were put into operation, as were industrial rubber and asbestos goods plants in the Belotserkovskiy association of tires and rubber and asbestos goods, the Ivano-Frankovskiy plant of fine organic synthesis. New capacities

have been established for production of about 450,000 tons of plastics and synthetic resins, over 1,000,000 tons of sulfur, about 1,300,000 tons of sulfuric acid, and over 3,000,000 tons of ammonia.

Chemists of the republic are hard at work to implement the main task of the 10th Five-Year Plan: further development of production efficiency and labor quality.

It is very important to note that the high rates of growth in production volume in chemical sectors have been achieved on a qualitatively new basis: by establishing plants of great unit capacity having a high degree of process automation, which make it possible to greatly enhance labor productivity; further intensification of oil re-processing, which facilitated an increase in the output of high-octane gasoline, lubricants, low-sulfur diesel and aviation fuels; and assimilation of production of several advanced products and articles.

It has been estimated that throughout the country as a whole, one ruble expended to manufacture and apply fertilizers yields a conventional net profit ranging from 2.5 to 3 rubles; using low-sulfur diesel fuel, the time between repairs of engines has increased 1.5-fold; with replacement of solidol by "Litol-24" lubricant, whose manufacture is organized by the Berdyanskiy petroleum and oil pilot plant, operating expenditures per transportation unit have been reduced 16 rubles per annum, which country-wide yields a savings of millions of rubles.

In the 10th Five-Year Plan, the republic's chemists mastered over 700 new kinds of products. More than 650 articles have been manufactured with the Seal of Quality. The relative share of high quality products versus the year 1975 has more than doubled and in chemistry now equals 26.9 percent, and 29.2 percent in petroleum refining and petrochemistry.

Work to increase quality was stimulated by the resolution of the Central Committee of the CPSU "On work experience of party organizations and staff of leading enterprises of the Lvov oblast in elaborating and incorporating a comprehensive system of quality control". At most enterprises, work is almost completed in establishing comprehensive quality control systems. Party organizations are making creative use, based on specific conditions, of the experience of leading groups in Lvov and Minsk, Moscow and Leningrad for further improvement and intensification of the systems approach to solving the quality problem.

Specialists from scientific-research and academic institutes of the republic have been drawn into this work. For example, the Khimprom association of Sumy is collaborating with more than 40 scientific organizations. In the 10th Five-Year Plan, the economic effect of new technology introduced came to 18,000,000 rubles. Several studies have been aimed at enhancing quality and, in consequence, high quality product output has more than doubled and its relative share now comes to 47 percent of the total product output.

The ever wider development of socialist competition, its orientation toward quality indicators, maintenance and promulgation of advanced experience were

named by comrade L. I. Brezhnev in his speech at the November 1979 Plenum of the CC CPSU among the primary trends of organizational and mass policy work of party organizations to solve current national economic problems. Experience shows that in those groups where party organizations have been able to transfer the center of organizational work directly to the primary labor groups, where they are hard at work carrying on a purposeful search for innovative forms of competitive organization, increased competitiveness and activity and have been able to develop methods of objective evaluation of the work results of each worker, they have found it easier to overcome problems, successfully deal with tight schedules and socialist obligations.

This type of work style is inherent, for example, in party committees of the Azot industrial association of North Donetsk, Dneproshina industrial association of Dnepropetrovsk, the Svema industrial association of Shostkino, the petroleum and oil plant and fiber glass plant of Berdyansk and the Monokristallreaktiv scientific-industrial association.

The staff of these enterprises have long worked stably, have successfully met state schedules and socialist competitions. The basic technical and economic indicators of their activity are at a level which in some cases even exceeds the five-year plan targets. They have repeatedly won the All-Union socialist competition and received the highest evaluation, awards of the Red Banner of the CC CPSU, USSR Council of Ministers, AUCCTU and the Komsomol Central Committee.

Valuable experience of organizing socialist competition to achieve specific goals has been gained at the Svema industrial association in Shostkino. The association staff greatly exceeded the control figures of the five-year plan's four-year level in terms of basic technical and economic indicators. Above-target production came to over 19,000,000 rubles, including some 88,000 meters of movie film and 320,000 meters of magnetic tape. The relative share of high quality products increased threefold over 1975. Today over 60 percent of the amateur movie film and magn tic tapes are produced with the State Seal of Quality.

At the Dneproshina association in Dnepropetrovsk, a comprehensive product quality control system and efficient utilization of material and labor resources have been introduced; this makes it possible to evaluate the labor quality and efficiency of all staff members, from the workers to the director. About 90 percent of the worker prizes are awarded for quality indicators; for technical engineering workers, the prize is split down the middle: one half is awarded for reaching targeted goals, and the other for the labor quality coefficient. Introduction of this system greatly improved labor organizations, enhanced socialist competition activities, and in consequence, raised the relative proportion of high quality products to 77 percent, a value of more than 16,000,000 rubles above plan, including hundreds of thousands of automotive tires.

Competition was wide-ranging here under the motto: "Stable cadres, high labor and social discipline for every collective". The birth of this initiative was preceded by a great deal of work on promulgating the team form of labor organization with a coefficient of labor participation; it had a positive effect not only

on the growth of labor productivity, but also on the improvement of the mental microclimate in the collectives and strengthening of cadres. In this five-year plan, the number of labor discipline violations in the association dropped to 40 percent of its prior level and labor turnover was reduced 30 percent; at the present time it is half as great as in the sector as a whole.

Without a doubt, in view of the requirements of the resolution of the CC CPSU, USSR Council of Ministers and AUCCTU "On further strengthening of labor discipline and reduction of labor turnover in the national economy", the work experience of the party organization of the Dneproshina association to enhance the educational function of socialist competition is worthy of careful attention and promulgation.

Workers of the republic's chemical sectors, inspired by decisions of the November, 1979 Plenum of the CC CPSU, L. I. Brezhnev's speech at the Plenum, struggling toward a worthy encounter of the 26th Congress of the CPSU and Lenin's anniversary, have taken on the obligation in the final year of the 10th Five-Year Plan to produce 142,000 tons of fertilizer, 50,000 tons of fuel oil, 45,000 tons of gasoline, 28,000 tons of sulfuric acid, 30,000 automotive tires and a large number of other products over and above the schedule.

Competition to fulfill planned assignments and socialist obligations ahead of schedule has opened up in all labor groups under the motto: "Perform like shock workers, work Lenin-style, in the final year of the five-year plan". By Lenin's anniversary, personal five-year plans were completed by over 400 industrial groups, about 9,500 leading workers and innovators of production. As always, the communists are the exemplary ones.

An honored position among these, by rights, belongs to G. D. Usatenko, winner of the order of the Red Banner of Labor, holder of the UkrSSR State Prize, and twistress of the fiber glass plant of Berdyansk; she was the first one in the country's chemical industry to complete her own five-year plan and by the 63rd anniversary of the Revolution, obligated herself to complete 15 annual quotas.

The initiator of the competition under the motto "Your own five-year plan for labor productivity within four years" was V. V. Galkin, winner of the order of the Red Banner of Labor, holder of the Prize imeni Lenin Komsomol, deputy of the UKrSSR Supreme Soviet and instrument control man of the Azot association of North Donetsk; he met his obligation ahead of schedule, within three years and three months. In the association alone, his initiative was supported by 730 persons: this yielded an economic profit of about 6,000,000 rubles.

The personal five-year plan of T. V. Vetokhina, winner of the "Badge of Honor", holder of the Prize imeni Lenin Komsomol, delegate to the 18th Congress of Komsomol, a cutter at the Svema industrial association, was completed in three years and four months. Before the end of the five-year plan, Tat'yana Vladimirovna took on the obligation to finish more than 60,000,000 meters of high quality magnetic tape above quota, worth about 250,000 rubles.

Many such examples could be given. On the whole, the work results for the elapsed period offer convincing proof that in the 9th Five-Year Plan, the chemical sectors

have taken yet another giant lead forward, increasing their role in the acceleration of scientific and technical progress and the solution of important national economic problems.

At the same time, one must recognize that the chemical sectors did not achieve the targeted level in terms of some indicators. Growth in production of fertilizers and certain other items was less than noted. The primary reasons for the shortfall are errors in planning, late start up of new production and unsatisfactory utilization of existing production at many enterprises. Capacities for production of fertilizers, sulfuric acid, ammonia and other products are not operating at full load. There are especially many unused reserves at the Rovno and Cherkassk association Azot, at the Lisichansk oil refining plant and at several other enterprises.

The decisions of the November 1979 Plenum of the CC CPSU and the resolution of the CC CPSU and USSR Council of Ministers on improving the management mechanism require a thorough turnabout of all our activities to enhance quality and efficiency, increase labor productivity, for maximum utilization of internal reserves existing at each enterprise, sections and work site. Organizational and political work of all party and social organizations and managers should now be directed toward achieving these goals.

Complex, critical problems face the republic's chemists in the coming year. The leading problem is to achieve a significant improvement in the use of equipment and thereby maximally reduce the lag behind assignments of the five-year plan in the production of mineral fertilizers and other chemical products. The program for capital construction is also strained. In 1980, large plants for productions of carbamide and dilute nitric acid must be put into operation in Dneprodzerzhinsk, Cherkassy and Gorlovka, sulfuric acid in Konstantinovka, calcined soda in Lisichansk and several other facilities. It is not only important to start up these capacities on time, but they must be assimilated as quickly as possible. From the very start of the 11th Five-Year Plan, the success of work will greatly depend on this.

Workers in the republic's chemical sectors have prepared a tremendous gift for their occupational holiday. In the first three months of 1980, 140,000 tons of fertilizers, thousands of tons of ammonia, thousands of automobile tires and a large quantity of other products were produced above the quota.

In view of the great political and labor upheaval required in preparation for the 26th Congress of the CPSU, the republic's chemists are hard at work completing the final year's plan of the 10th Five-Year Plan ahead of schedule.

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UNIT FOR PROCESSING HELIUM

Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 2, Feb 81 pp 5-7

KALASHNIKOV, I. P.

[Abstract] Because of its size and novel technology, the helium plant designed by the Sumy Mechanical Engineering Industrial Association imeni M. V. Frunze was awarded the 1980 State prize. The plant was designed to handle large volumes of natural gas containing at least 0.055% helium and it has two major innovations which improve efficiency. The first is an increase in the overall size of each component in the operating line (the pipe diameters were almost doubled, resulting in a 3.5-fold increase in capacity). The second is a decrease in the size of the tubing in the heat-exchangers, which in turn increases the surface area. Plant capacity was closer to 3.0×10^9 m^3/yr than to the initially calculated volume of about half that amount. At the present time, the first two high-efficiency installations for helium production have been put in operation at the Orenburg helium plant. The next stage in the program to obtain helium will be discussed at the 26th CPSU Congress.
[76-12027]

UDC 534.222.2

STRUCTURE OF DETONATION FRONT OF DISPERSED SOLID EXPLOSIVE COMPOUNDS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 256, No 6, 1981
(manuscript received 24 Jul 80) pp 1409-1411

DANILENKO, V. A. and AFANASENKOV, A. N., Institute of Chemical Physics, USSR Academy of Sciences, Moscow, and Institute of Electrowelding imeni Ye. O. Paton, USSR Academy of Sciences, Kiev

[Abstract] An experimental investigation of the title topic was carried out using the following explosive compounds: a mixture of compounds based on ammonium nitrate, a powder composed of trinitrotoluene and trimethylenetrinitramine having a grainsize of 4-5 mm and, also, a mixture of regular trimethylenetrinitramine with an inert additive. From photographs of the detonation front, it was established that the brightest areas occurred in a narrow band adjacent to the front. The pulsation frequency of the front is about 300 kHz for the ammonium nitrates in diesel, 1 to 5 mHz for the mixtures of trinitrotoluene with the ammonium nitrates, and 60 mHz for trimethylenetrinitramine. Values are also given for the average size of the cell, the angle of inclination of the cell wall to the direction of detonation, and the Strukhal number. In general, the detonation wave of the compounds investigated is pulsating and has a regular cell structure as a characteristic feature of the wave front. This regular cell structure indicates that the hypothesis of isotropic turbulence is not supported for these compounds. Figures 3; references 13: 9 Russian, 4 Western. [71-12027]

UDC 539.194+547.024

THEORETICAL POLARITY CRITERIA IN STUDYING REACTIVITY OF PHOSPHINYL RADICALS

Kiev TEORETICHESKAYA I EKSPERIMENTAL'NAYA KHIMIYA in Russian Vol 17, No 4, Jul-Aug 81 (manuscript received 16 Oct 80) pp 531-534

PEN'KOVSKIY, V. V., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] A quantum chemical approach was employed in study of the interaction of phosphinyl radicals ($P(CH_3)_2$, PH_2, and PF_2) with ethylene and its fluorine derivatives to delineate the relationship between the polarity of a radical and the energy of the vicinal orbital radical-substrate interactions following Volovik's derivation (Volovik, S. V., et al., Teoret. i Eksperim. Khimiya, 16(1): 107-113, 1980). The results demonstrated that radical nucleo- or electrophilicity determined the course of the reaction when a double bond or intramolecular cyclization is involved; furthermore, the most reliable empirical information was provided by evaluation of the energy of the outer filled orbitals of the reactants. References 14: 6 Russian, 8 Western.
[156-12172]

UDC 541.49+542.61+547.242.04

STRUCTURE AND ELECTRON DONOR PROPERTIES OF TERTIARY ARSINE OXIDES

Moscow USPEKHI KHIMII in Russian Vol 53, No 5, May 81 pp 860-888

LASKORIN, B. N., YAKSHIN, V. V. and LYUBOSVETOVA, N. A.

[Abstract] This is a survey-type report. The interest in organic arsine compounds underwent recently an explosive revival due to the discovery of their use in several technological fields. The literature accumulated on these compounds had not been surveyed systematically, thus limiting the utility of these compounds in complex formations and in the extraction processes. This review has attempted to fill this void. The authors analyzed the electronic structure and spacial orientation of arsine oxides, addressing the transfer of various effects from the radical portion of the molecule through the arsenic atom to the reactive center. Principal attention is devoted to complex formation and to the extraction processes involving inorganic acids and metal salts. A separate section is devoted to the basicity of arsenic containing extraction reagents in aqueous and non-aqueous solutions. It is concluded that arsine compounds differ from organophosphoric analogues because of their electronic and spacial characteristics. Their applicability in the purification of aqueous solutions from radioactive and toxic elements has shown a promising future. Further studies may find application in analytical and in coordination chemistry as well as in hydrometallurgical adsorption-extraction processes. References 274: 97 Russian, 177 Western. [111-7813]

UDC 541.67

DIPOLE MOMENTS OF ORGANOPHOSPHORUS COMPOUNDS, COMMUNICATION 20: DIPOLE MOMENTS, KERR CONSTANTS AND CONFORMATIONS OF PHOSPHONIC ACID DIFLUORIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81
(manuscript received 16 Jun 80) pp 985-989

PATSANOVSKIY, I. I., ISHMAYEVA, E. A., LEVIN, Ya. A., GILYAZOV, M. M. and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin; Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch of the Academy of Sciences

[Abstract] A series of $F_2P(O)R$ difluorides was studied by the methodology of dipole moments and Kerr constants, where R was CH_3 (I), tert-C_4H_9 (II), CH_2= CH (III), trans-C_6H_5CH=CH (IV), CH_2Cl (V) and cyclo-C_6H_{11} (VI). The difluoride III was found to be in a conformational equilibrium with predominance of the cis form (70%). The analogue IV existed principally in the trans form; this stabilization was due to intramolecular electronic interaction involving the phosphorus atom, because it was possible that the longer chain in IV made this interaction feasible. The derivative V behaved analogously to phosphonic acid dichloride in that it exists in trans-gosh conformational equilibrium, where the orientation of P=O and C-Cl groups was predominantly trans. Substitution of Cl by F had no effect on this. References 39: 25 Russian, 14 Western. [109-7813]

UDC 541.67

DIPOLE MOMENTS OF ORGANOPHOSPHORUS COMPOUNDS, COMMUNICATION 19: CONFORMATION OF N-SUBSTITUTED 1,3,6,2-DIOXAAZAPHOSPHOCYNANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81 (manuscript received 26 Jun 80) pp 980-985

PATSANOVSKIY, I. I., ISHMAYEVA, E. A., D'YAKOV, V. M., REMIZOV, A. B., KUZNETSOVA, G. A., LAZAREV, I. M., VORONKOV, M. G. and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov,Lenin; Irkutsk Institute of Organic Chemistry, Siberian Branch of the USSR Academy of Sciences

[Abstract] Physical properties and spacial structures of N-substituted dioxaazaphosphocynanes $CH_3P(O)(OCH_2CH_2)_2NR$ (where R = CH_3, C_4H_9 and C_4H_5) were studied by means of their dipole moments, Kerr effects and the IR and PMR spectroscopy. Six conformations were possible for the dimethyl substituted derivative with different axial and equatorial orientations of the exocyclic N-CH_3 and P=O bonds. The results obtained showed that there is no appreciable N•P interaction in these compounds. In liquid state, the methyl analogue exists in a crown•chair-boat (lea•3aa) conformational equilibrium, in about a 40:60 ratio. In crystalline state, all three compounds exist only in the crown conformation with an axial P=O. Figures 2; references 28: 10 Russian, 18 Western. [109-7813]

UDC 547.(241 + 231 + 239)

SYNTHESIS OF OXIMINOCYANOMETHYLPHOSPHONATES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81 (manuscript received 24 Oct 80) pp 1206-1207

STREPIKHEYEV, Yu. A., KHOKHLOV, P. S. and KASHEMIROV, B. A., Moscow Chemical-Technological Institute imeni D. I. Mendeleyev

[Abstract] To a mixture of 7.45 g O,O-dimethylcyanomethylphosphonate and 4.45 g propylnitrite cooled to -10°C, a solution of 1.15 g sodium in 40 ml absolute alcohol is added dropwise. The reaction mixture is kept for 6 hrs at 0°C, the solvent is removed and the residue is dissolved in cold water, washed with ether, acidified to pH 5 and extracted with ether. After removal of the solvent, the residual oil crystallizes, to yield O,O-dimethyloximinocyanomethylphosphonate was obtained, n_D^{20} 1.4511, d_4^{20} 1.220. References 1 (Russian).
[109-7813]

UDC 547.26'118

ADDITIVE EFFECT OF SUBSTITUENTS OF TETRACOORDINATED PHOSPHORUS ATOM

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81
(manuscript received 9 Jun 80) pp 1205-1206

GUBAYDULLIN, M. G.

[Abstract] In an earlier study it was shown that there is an additive effect of the substituents of phosphoric acids on the substitution reactions. This conclusion was questioned by Baranskiy and Istomin, because the logarithms of the reaction rate constants of alkaline hydrolysis did not pass through the zero point, even though it showed a linear trend. Other authors have also reached the conclusion about the additive character of the substituent effects, but their equations did not support these conclusions. An argument has been proposed against the explanation used by these authors that a p_π-d_π-conjugation is responsible for the additive effect. References 4 (Russian).
[109-7813]

UDC 547.496.3

SYNTHESIS AND Z,E-ISOMERIZATION OF S-METHYL-N-TERT-BUTYL-N'-DIETHOXYPHOSPHORYLISOTHIOUREA

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81
(manuscript received 21 Oct 80) pp 1203-1204

BOGEL'FER, L. Ya., GRAPOV, A. F., NEGREBETSKIY, V. V., ZONTOVA, V. N. and MEL'NIKOV, N. N., All-Union Scientific Research Institute of Chemical Plant Protective Agents

[Abstract] Spacial structure and Z,E-isomerization of S-methyl-N-tert-butyl-N'-diethoxyphosphorylisothiourea (I) were studied. The stability of Z-isomer (syn) is affected by two opposing factors: intramolecular H-bonding and the repulsive forces between the CH_3S and tert-C_4H_9 groups. In $CDCl_3$ solution, at -30°C, I exists in a 9:1 mixture of Z:E isomers. In CD_3OD, the equilibrium is shifted toward the E-isomer (Z = 10%, E = 90%). In a mixture of $CDCl_3$ and CD_3OD, the equilibrium is on an intermediate level. References 2 (Russian).
[109-7813]

UDC 547.341

PHOSPHORYLATION OF TERTIARY AMIDES WITH PHOSPHORUS PENTACHLORIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81
(manuscript received 22 Oct 80) pp 1201-1202

PENSIONEROVA, G. A., ROZINOV, V. G. and GLUKHIKH, V. I., Irkutsk State University imeni A. A. Zhdanov; Institute of Petro- and Carbo- Chemical Synthesis at the Irkutsk State University

[Abstract] Tertiary amides can be easily phosphorylated with PCl_5 when their R and R' substituents have electron accepting properties. For example, PCl_5 reacted with diphenyl acetamide at 10-15°C in benzene to give a 65% yield of β-diphenylamino-β-chlorovinylphosphonic acid, m.p. 81°C. With dialkylacetamide, PCl_5 yields but a tarry reaction mixture. References 3: 2 Russian, 1 Western.
[109-7813]

UDC 547.26'118:547.458

SYNTHESIS OF WATER SOLUBLE POLYSACCHARIDES CONTAINING AMINOALKYL DERIVATIVES OF THIOPHOSPHORIC ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81
(manuscript received 24 Jul 80) pp 1196-1201

BONDAREV, G. N., ISAYEVA-IVANOVA, L. S. and KRIVENKOVA, S. N., Leningrad Institute of Nuclear Physics imeni B. P. Konstantinov, USSR Academy of Sciences

[Abstract] Aminoalkylthiophosphate derivatives of dextrose were synthesized from S-[N-(3-aminopropyl)-2-aminoethyl]-thiophosphoric acid, sodium S-(2-aminoethyl)thiophosphate and dialdehyde derivatives of dextrose with molecular weights of 20, 40, 60 and 110 thousands. The yield of the reaction was not dependent on molecular weight All compounds were water soluble, the solubility decreasing somewhat with increasing MW. The most effective way to isolate the product was based on a dialysis followed by lyophilization. It was established that each fragment of the dialdehyde dextran reacted with two molecules of thiophosphoric acid derivatives. Figures 2; references 10: 6 Russian, 4 Western.
[109-7813]

UDC 547.26.118:547.551.43

INVESTIGATING REACTION OF DIALKYLPHOSPHITES WITH ISOCYANATES BY METHOD OF IR SPECTROSCOPY

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81 (manuscript received 9 Jul 79) pp 1035-1042

BAKHITOV, M. I., ZHARKOV, V. V., KUZNETSOV, Ye. V. and KLIGMAN, F. L., Kazan' Chemical-Technological Institute imeni S. M. Kirov

[Abstract] The reaction of dialkylphosphites with isocyanates in absence of catalytic reagents is a complex process consisting of parallel and sequential reactions. The intermediate products can react with the starting compounds as well. This reaction was investigated by an IR spectroscopic method using diethylphosphite and phenylisocyanate as the starting materials. The products of this reaction included phenylamide of diethylphosphoneformic acid, CO_2, diphenylcarbodiimide and its decomposition products. To verify the participation of the P=O group from the diethylphosphorous acid in the formation of CO_2, phenylisocyanate was reacted with diethylthiophosphorous acid; in this case instead of CO_2, COS was obtained. Figures 5; references 14: 12 Russian, 2 Western.
[109-7813]

UDC 547.1'118

IMINODI(METHYLENEPHOSPHONIC) ACID AND ITS REACTIVITY

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81 (manuscript received 1 Sep 80) pp 1028-1035

TSIRUL'NIKOVA, N. V., TEMKINA, V. Ya., SUSHITSKAYA, T. M. and FYKOV, S. V., All-Union Scientific Research Institute of Chemical Reagents and Ultra Pure Chemical Compounds

[Abstract] A new synthetic method was developed for iminodi(methylenephosphonic) acid (I) based on oxidative destruction of N,N-hydrazinedi-(methylenephosphonic) acid. Another method for the synthesis of I employed thermal or electrochemical dealkylation of nitrilotri-(methylenephosphonic) acid, the latter method giving higher yield with less impurities. The reactivity of I in Mannich reaction and in halogen substitution reaction was investigated, showing that I could be used in the substitution reactions, but that, in the Mannich reactions, only low yields were obtained due to a competitive reaction with formaldehyde. References 16: 8 Russian, 8 Western.
[109-7813]

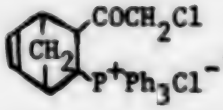
UDC 547.558.1

SYNTHESIS AND PHYSICAL-CHEMICAL PROPERTIES OF OXOVINYLTRIPHENYLPHOSPHONIUM- AND OXOVINYLTRIETHYLAMMONIUM CONTAINING COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81
(manuscript received 17 Jun 80) pp 1024-1028

SHEVCHUK, M. I., RUDI, V. P., MEGERA, I. V. and NADTOCHIY, F. A., Chernovtsy State University

[Abstract] In connection with recent discovery of surface active properties of phosphonium compounds, physical-chemical properties of a number of phosphonium and ammonium salts were determined. The following compounds were synthesized for this purpose: triethylammonium chloride of 4-chloro-1-butene-3-one, 1,4-bistriethylammonium chloride of 2-butene-3-one,

$[(C_6H_5)\ P^+CH{=}CHCOCH_2Cl]Cl^-$,  , $[(C_6H_5)_3P^+CH{=}CHCOCH_2N^+(C_2H_5)_3]Cl_2^-$,

triethylammonium chloride of 4-triphenylphosphonium chloride 2-butene-3-one, triphenylphosphoniummethyl-β-triphenylphosphoniumchlorovinyl ketone chloride, diethoxymethylphosphonate of β-triphenylphosphoniumchlorovinyl ketone, dibutoxymethylphosphonate of β-triphenylphosphoniumchlorovinyl ketone, and $Ph_3P^+CH{=}CHC(CH_2Cl){=}NNHAR$, where AR = $2,4\text{-}(NO_2)_2C_6H_3$ or $4\text{-}NO_2\text{-}C_6H_4$. The following properties were determined: the degree of hydrolysis, surface activity, electro-kinetic potential, critical concentratio- for the formation of mycellae and specific electric conductivity. Figures 1; references 3 (Russian) [109-7813]

UDC 547.558.1:831

ACYLPHOSPHONIUM SALTS IN ORTOLEVA-KING REACTION

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81
(manuscript received 24 Jun 80) pp 1020-1024

CHERNYUK, I. N., SHEVCHUK, M. I., YAGODINETS, P. I. and VOLYNSKAYA, Ye. M., Chernovtsy State University

[Abstract] Triphenylphosphonium salts were condensed with iodine and heterocyclic compounds according to the reaction:
$\bar{X}(C_6H_5)_3P^+\text{-A-}\overset{\overset{\cdot\cdot}{O}}{\overset{|}{C}}\text{-}CH_3 + I_2 + 2B \rightarrow \bar{X}(C_6H_5)_3P^+\text{-A-}\overset{\overset{\cdot\cdot}{O}}{\overset{|}{C}}\text{-}CH_2B^+I^- + HI\cdot B^+$ (where
A = $-CH_2-$, $-CH(CH_3)-$, $p\text{-}C_6H_4-$, $p\text{-}CH_2C_6H_4-$; X = I^-, ClO_4-; and B = pyridine, quinoline, triethylamine). The reaction was carried out in an excess of

heterocyclic bases which were used as solvents and reagents. The reaction time was controlled by the disappearance of the iodine color. The reaction with pyridine and quinoline had to be heated to 70-80°C for 6-10 hrs; with triethylamine it needed only room temperature and absolute alcohol as the solvent. The UV and IR spectra of the products obtained are reported. References 11: 8 Russian, 3 Western.
[109-7813]

UDC 547.26'118

IMIDE-AMIDE REARRANGEMENT OF IMIDOTHIOPYROPHOSPHATES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81
(manuscript received 15 Jul 80) pp 1015-1020

TUPCHIYENKO, S. K., DUDCHENKO, T. N. and GOLOLOBOV, Yu. G., Institute of Organic Chemistry, UkSSR Academy of Sciences

[Abstract] Reaction of amidodiethylphosphites with diethoxyphosphorylsulfenyl chlorides (I) should lead in the first stage of the reaction to the formation of a quasiphosphonium salt which in presence of NEt_3 should break down to an imidothiopyrophosphate. When N-alkyl(aryl) amido-O,O-diethylphosphites were reacted with I in presence of NEt_3, the expected O,O-diethyl-[N-alkyl(aryl)-N-diethoxyphosphoryl]amidothiophosphates (II) could not be isolated in pure state due to decomposition during the distillation. In addition, however, small quantities of O,O-dialkyl-[N-alkyl(aryl)-N-diethoxyphosphoryl]amidothiophosphates, the rearrangement products of II were obtained. The ease of rearrangement correlated with the nucleophilicity of the imine nitrogen atom. References 8: 6 Russian, 2 Western.
[109-7813]

UDC 541.6:547.8

SPACIAL STRUCTURE OF PHOSPHORUS-CONTAINING HETEROCYCLES, COMMUNICATION 25: INTRAMOLECULAR ELECTRONIC INTERACTION IN 2-X-1,3,2-DIHETEROPHOSPHORINANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81
(manuscript received 24 Jun 80) pp 1007-1014

ARSHINOVA, R. P., Scientific Chemical Research Institute imeni A. M. Butlerov, Kazan' State University imeni V. I. Ul'yanov-Lenin

[Abstract] Among the cyclic compounds of trivalent phosphorus the 2-X-1,3,2-diheterophosphorinanes have been investigated most thoroughly. Their spacial structure is stabilized in a chair conformation with X in the axial orientation. Changing the substituent X leads to considerable shifts in

electronic density of the phosphorus-containing portion of the molecule. The polarizability of P-O and P-X bonds undergoes extensive anisotropic changes related to the acceptor properties of X. The P-Cl bond length increases in the series of O<S<N substituents. All of this indicates high electronic lability of the Y_2PX group, which in turn is explained by the p-σ^* hyperconjugation magnified by the field effect and α-effect of the separation of adjacent unshared electron pairs of the heteroatoms. In its turn, the intensity of the shifts in the electronic cloud of the unshared electron pair, the degree of bond weakening and the change in the ellipsoid of its polarizability depend on conformational parameters and on the location of the heteroatom in the periodic table. In general, combination of trivalent phosphorus with various heteroatoms leads to an electronically-labile system with an ability to alter the electronic cloud. This property is a result of two interacting effects: the destabilization of the p-p interaction (α-effect) which favors acceptor properties in the bonds, and p-σ^* hyperconjugation which is intensified by the first effect. Figures 2; references 32: 22 Russian, 10 Western.
[109-7813]

UDC 547.241

COMPARATIVE REACTIVITY OF O,O-DIMETHYLPHOSPHONO- AND PHENYLSULPHENYLCHLORIDES IN ADDITION REACTION WITH VINYLSILANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81 (manuscript received 8 Sep 80) pp 1003-1007

KUTYREV, G. A., VINOKUROV, A. I., ISTOMIN, B. I., CHERKASOV, R. A. and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin; Irkutsk State University

[Abstract] Kinetics of the addition of O,O-dimethylphosphono- and phenylsulfenyl chlorides to vinylsilanes was investigated. It was established that, analogously to the reaction with styrene, the introduction of a phosphone group leads to a change in the factors determining the rate-controlling step in this reaction. In the case of the organophosphorus compounds, the dominant process is the shift of electronic density from the double bond of the unsaturated compound toward the sulfur atom of the sulfenyl chloride, with formation of an intermediate π-complex or a σ-sulfone. In the case of the aromatic analogues, the important step is the break of the S-Cl bond leading to the formation of an ionic pair structure of the activated complex. A similar change in the character of the intermediate state was observed with olefines which had different π-donor properties. The coordination of donor fragments of the electrophile with silicon containing substituent in the unsaturated partner plays an important role in forming the activated complex. Figures 2; references 16: 11 Russian, 5 Western.
[109-7813]

UDC 547.26'18

REACTIONS OF ISOCYANATES AND ISOTHIOCYANATES OF TRICOORDINATED PHOSPHORUS ACIDS WITH α-HALOCARBONYL COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81
(manuscript received 18 Jul 80) pp 995-999

KONOVALOVA, I. V., BURNAYEVA, L. A., NOVIKOVA, N. K., KEDROVA, O. S. and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin

[Abstract] Mono- and diisothiocyanatophosphites react with α-halocarbonyl compounds only by the Perkov reaction to yield vinyl esters of iso(diiso)thiocyanophosphonic acid. When dimethyl- and diethylisothiocyanophosphite was reacted at 0 to -5°C with an ethyl ester of chloropyruvic acid in absence of a solvent, O-alkyl-O-(α-carboalkoxyvinyl) ester of isothiocyanophosphoric acid was formed. It was further shown that methyldiisothiocyanophosphite reacts with the esters of chloro- and bromopyruvic acids at 25-30°C in absence of solvents yielding α-carboethoxyviny' ester of diisothiocyanophosphoric acid. The reaction of monoisocyanate and monoisothiocyanate of dimethylphosphorous acid with hexachloroacetone occurs only along the Perkov's rearrangement path yielding O-methyl-O-(α-trichloromethyl-β, β-dichlorovinyl) esters of isocyano- and isothiocyanophosphoric acids. In contrast to this, hexafluoroacetone reacts with diethylisocyanophosphite to yield 2,2-dimethoxy-4-oxo-5,5bistrifluoromethyl-1,3,2-oxazaphosphol-2-ene. References 4: 3 Russian, 1 Western.
[109-7813]

UDC 547.26'118

REACTIONS OF DIALKYLPHOSPHOROUS ACID ISOTHIOCYANATES WITH IMINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 51, No 5, May 81
(manuscript received 11 Jul 80) pp 993-995

KONOVALOVA, I. V., CHERKINA, M. V., YARKOVA, E. G., BURNAYEVA, L. A. and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin

[Abstract] Reactions of imines with dialkylisothiocyanatophosphites (I) were studied, reacting N-methylbenzaniline, N-phenyl- and N-methyltrichloroethylidenimines with dimethyl and diethyl esters of isothiocyanatophosphorous acid. Equimolar quantities of these reagents were reacted at room temperature with or without any solvent (ether, benzene or methylene chloride were used as solvents). The products were viscous liquids from which crystalline 1:1 addition products were isolated. In the reaction of dimethylisothiocyanatophosphite with N-methyltrichloroethylidenimine, a hydrolysis product of the intermediate compound with the P=N bond was isolated: 1-methyl-2-trichloromethyl-3-methoxy-3-oxo-5-thione-1,4,3-diazaphospholane. When I was reacted with imines containing labile hydrogen atom such as diphenylketimine or benziminoethyl ester, the products were the substituted iminium thiocyanates. References 8: 7 Russian, 1 Western.
[109-7813]

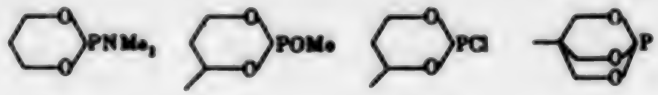
UDC 543.42:547.1.118

PHOTOELECTRIC SPECTRA OF DI- AND TRIESTER ACIDS OF TRIVALENT PHOSPHORUS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 256, No 6, 1981
(manuscript received 4 Sep 80) pp 1412-1415

ZVEREV, V. V., VILLEM, Ya. Ya. and ARSHINOVA, R. P., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, USSR Academy of Sciences, Kazan'

[Abstract] The title study was carried out on triethylphosphite (I), diethylphenylphosphinite (II), substituted 2-X-1,3,2-dioxaphosphorinanes (III-V), and a bicyclic form (VI) in order to establish consistent values for



III IV V VI

the interpretation of the ionization potential (IP) of this type of structure. Several spectra are shown and the IP values, together with the rationale for their derivation, are presented. In the series of compounds III, IV, and V, the symbate increase in the energy of all the upper occupied orbitals is a function of the charge transfer from the atoms in the ring to the exocyclic substituent for the latter two groups and the reverse for group III. These trivalent phosphorus compounds do not appear to follow the rule that the IP's of the η_p orbital characterize the proton's behavior, such as its basicity and ease of complex formation inasmuch as their basicity increases in the order VI IV I, which is the opposite of the trend suggested from the normal values of the IP. Figures 2; references 13: 7 Russian, 6 Western.
[71-12027]

UDC 63:54

TOXICOLOGICAL GROUP AT LENINGRAD OBLAST AGROCHEMICAL LABORATORY

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian Vol 18, No 10, Oct 80 pp 9-11

ZHURAVLEVA, I. P., candidate of biological sciences, ANDREYEVA, Ye. P. and BUROBINA, G. S., Leningrad Oblast Agrochemical Laboratory

[Abstract] The title group evaluates the accumulation of persistent pesticides in agricultural soils and the contamination of vegetables by nitrates and nitrites. An example of the first task is the program set up in 1976 to monitor levels of hexachlorocyclohexane (HCCH) which had been widely used on vegetable and fodder crops. Its build-up in the soil and the mechanisms for degradation and loss were established. This allowed a program to be developed for the safest and most effective use of this pesticide. The second evaluative task, initiated in 1979, was to monitor plants for excessive amounts of nitrates and nitrites, derived from heavy fertilizing with nitrogen-rich materials. One study showed that 31% (or 201) of the 631 samples analyzed contained significant amounts of nitrates. References 3 (Russian).
[74-12027]

UDC 662.67

BITUMINOUS CHARACTERIZATION OF BULGARIAN OIL SHALE FROM BOROV DOL DEPOSITS

Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 30, No 2, Apr-Jun 81 (manuscript received 8 Sep 80) pp 69-74

KLESMENT, I., KUUZIK, MARET and POBUL', LINDA, Institute of Chemistry, ESSR Academy of Sciences

[Abstract] Oil shale deposits are widely disseminated in Bulgaria. The deposits in Borov Dol are of commercial potential; the goal of this study was to determine precisely the composition of Borov Dol bitumen. A sample analyzed contained 2.8% CO_2, 2.3% total sulfur and 20.3% of organic compounds. Extraction of the crude yielded bitumen A (consisting of hydrocarbons, sulfur containing compounds and acids) and bitumen C (consisting almost entirely of acids). Bitumen A contains straight chain C_{14}-C_{33} normal paraffins, many of which had an odd number of carbon atoms. They are well-preserved wax residues from various plants. Both bitumens contain C_{11}-C_{28} fatty acids, in which the C_{22} and C_{24} acids predominate. It was concluded that biological transformation processes did not affect the original plant material to any significant degree. Figures 3; references 9: 5 Russian, 4 Western.
[114-7813]

UDC 662.73

STUDY OF BALKHASHITE, COMMUNICATION I: COMPOSITION OF BITUMEN

Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 30, No 2, Apr-Jun 81 (manuscript received 8 Sep 80) pp 75-83

POBUL', LINDA and KLESMENT, I., Institute of Chemistry, ESSR Academy of Sciences

[Abstract] One of the intriguing problems in organic geochemistry is the genesis of combustible minerals of the sapropelite type. The peat stage of the fossilization of algae is exemplified by two caustobioliths: coorongite (Australia) and balkhashite (Central Asia). Formation of balkhashite could

still be seen at the beginning of this century; it stopped accumulating when the water pattern in Lake Balkhash changed. The starting material for balkhashite consisted of algae Botriococcus Braunii. Dead plancton underwent anerobic diagenesis at the bottom of the lake, then the waves would wash it ashore, where the conversion was completed under oxidative conditions. The present article describes a comprehensive investigation of balkhashite, including its genesis. Three types of balkhashite were analyzed: 1) dark brown material collected from sites close to the current shore line, 2) grayish-black balkhashite from elevated areas and 3) scattered organic material collected from the lake shore sand. The following structural characteristics of balkhashite were established: slight predominance of paraffins with odd carbon number and acids with an even carbon number. Olefines have been found in it as well as a high content of a monobasic C_9 acid and some dibasic acids. The content of cyclic isoprene hydrocarbons is rather high, while the level of acyclic branched hydrocarbons is low. It was concluded that the starting material must have undergone considerable bacterial transformation, so that balkhashite was formed from secondary products. The composition of the scattered organic material was different from balkhashite, resembling much more closely the composition of algae. Figures 4; references 13: 3 Russian, 10 Western.
[114-7813]

UDC 546.22:614.841.47:622.67

TAR FROM SPONTANEOUSLY IGNITING DICTYONEMA OIL SHALE, COMMUNICATION 1: SULFUR IN TAR

Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 30, No 2, Apr-Jun 81 (manuscript received 29 Jul 80) pp 95-100

VESKI, R. and SIDOROVA, S., Institute of Chemistry, ESSR Academy of Sciences

[Abstract] The tendency of dictyonema combustible minerals toward self-ignition has been known from the laboratory experiments and from practical field experience. Analysis of the tar from self-igniting dictyonema oil shale is reported in this paper. The samples for this analysis were collected from the areas secreting gases around dumps and open pits from spent and from active fields. The extracted samples contained large amounts of sulfur in form of pyrites, sulfates and organic sulfur compounds. In comparison to the semicoking oil, the tars analyzed contained higher levels of elemental sulfur and oxygen. In the undergound combustion, sulfur can be formed from the breakdown of pyrite or by oxidation of the H_2S with air oxygen at the exit from the underground or even by oxygen dissolved in water. Figures 1; references 17: 11 Russian, 6 Western.
[114-7813]

UDC 9839474.40;665.7.032.57

TAR FROM SPONTANEOUSLY IGNITING DICTYONEMA OIL SHALE, COMMUNICATION 2: CHARACTERISTICS OF TAR'S CHEMICAL COMPOSITION

Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 30, No 2, Apr-Jun 81 (manuscript received 21 Nov 80) pp 101-105

UROV, K. and VYSOTSKAYA, V., Institute of Chemistry, ESSR Academy of Sciences

[Abstract] The products of self-igniting shale enter the environment and therefore can have detrimental effect on the biosphere. To estimate that danger, detailed chemical analysis of the tar being formed in this process was performed. The results showed that products forming during the combustion of dictyonema oil shale have an undesirable contaminating effect. Along with volatile organic compounds such as alkylated benzenes and organic sulfates which contaminate the atmosphere, the tar contains many polycyclic aromatic hydrocarbons, including carcinogens, along with their oxygenated and sulfur derivatives. The effect of these latter compounds on living organisms has not been evaluated adequately as yet. These compounds could become serous contaminants of the soil and ground waters. Figures 2; references 5: 4 Russian, 1 Western.
[114-7813]

UDC 662.613.4

TAR FROM SPONTANEOUSLY IGNITING DICTYONEMA OIL SHALE, COMMUNICATION 3: COMPOSITION OF SLOWLY BURNING TAR

Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 30, No 2, Apr-Jun 81 (manuscript received 17 Dec 80) pp 150-152

KLESMENT, I. and KUUZIK, MARET, Institute of Chemistry, ESSR Academy of Sciences

[Abstract] The tar sample for this analysis was collected at a burning dump of dictyonema shale, removed during the mining of phosphate rock. At the collection site, the surface temperature of the gas did not differ much from the surrounding air temperature. With increasing depth of sampling, temperature increased considerably. The extracted sample consisted of the bitumen of the starting shale and the tar froming due to the exposure to high temperature. At the surface the tar content was low, at the middle depth it reached a maximum of about 10% (probably as a result of migration) and then dropped again. The tar contains many acid components, some sulfur and no olefines; it resembles the composition of the bitumen much more than that of the common semicoking tar. It was concluded that this is due to the slow process of thermal destruction. Figures 1; references 4: 3 Russian, 1 Western.
[114-7813]

UDC 63:54

CHEMICAL-TOXICOLOGICAL DEPARTMENT IN IRKUTSK OBLAST AGROCHEMICAL LABORATORY

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian Vol 18, No 10, Oct 80 pp 11-12

ZHITOV, V. V., KREST'YANINOVA, N. G., LOSHKARYEVA, F. I. and SOKOLOVA, N. F., Irkutsk Oblast Agrochemical Laboratory

[Abstract] The title department was established in June, 1974. One of its early projects was evaluating residual amounts and studying the degradation and accumulation of organochlorine pesticides, such as hexachlorocyclohexane, metaphos, chlorophos and 2,4-D and corresponding values for nitrates. These studies were carried out using thin layer chromatography, gas chromatography, and potentiometric analyses. In 1978-79, a study was made of the effect of degradation of the amine salt of 2,4-D in the soil on wheat seedlings. Soil samples were taken both from an upper layer (0-20 cm) and lower layer (20-40 cm) in order to evaluate the ability of the pesticides and their degradation products to migrate. Techniques for measuring soil nitrates with an ion-selective electrode were developed in order to establish a rapid field method for assessing and monitoring nitrates in the soil. A project was begun in 1979 to measure nitrate concentrations of the productive areas of some truck gardens. References 3 (Russian).
[74-12027]

UDC 661.715.352

STATE OF AND PROSPECTS OF DEVELOPMENTS IN PRODUCTION OF BASIC SYNTHETIC RUBBER MONOMERS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D.I. MENDELEYEVA in Russian Vol 26, No 3, May-Jun 81 pp 252-258

STEPANOV, G. A., candidate of technical sciences, Scientific Research Institute of Monomers for Synthetic Rubber, Yaroslavl'

[Abstract] Recent advances in the production of butadiene, isoprene, styrene and isobutylene are reviewed. Currently all styrene and alpha-methylstyrene, two thirds of isoprene and more than half of butadiene are produced by dehydration of hydrocarbons, but use of oxidative dehydration with oxygen has been increasing. Much research has been done on the economic one-stage dehydration of butane and isopentane with the use of catalysts (e.g., chromo-alumina, DV-3M6 and 1M-612). Improvements in dehydration reactor design include the use of section units with fluidized beds, adiabatic reactors, units with circulating powdered catalysts and isothermal tube reactors. Advances have also been made in equipment and processes for extracting and purifying monomers by traditional mass-exchange methods. Extractive distillation of C_4 and C_5 fractions with polar solvents (e.g., acetonitrile, dimethylformamide, N-methylpyrrolidone and dimethylacetamide) has increased productivity and reduced costs. New processes for extracting isobutylene include the use of sulfuric acid, water and ion-exchanger catalysts. A two-stage process for obtaining isoprene from isobutylene and formaldehyde with the use of proton and dioxane catalysts is widely used, but a one-stage process with total conversion of formaldehyde has been recently patented. An original three-stage synthesis of isoprene from isopentane has been developed in the USSR, which reduces energy consumption by 35% in comparison with two-stage dehydration. Some other methods for obtaining monomers include dimerization of ethylene and the disproportionation of propylene to obtain cheap butenes, copolymerization of ethylene and propylene or their combined disproportionation to obtain inexpensive pentenes for dehydration to isoprene, and synthesis of isoprene from 2-butene and synthesis gas. References 34: 25 Russian, 9 Western.
[104-9307]

UDC 678.7(0.47)

FIFTY YEARS OF SYNTHETIC RUBBER PRODUCTION

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D.I. MENDELEYEVA in Russian Vol 26, No 3, May-Jun 81 pp 244-246

SOKOLOV, S. V., professor, Division of Thermostable Polymers, All-Union Scientific Research Institute of Synthetic Rubber im. S. V. Lebedev

[Abstract] A brief review of the history, types, production, properties and application of synthetic rubbers is presented. Major trends in the synthetic rubber market and production in the USSR, Japan and the USA are analyzed. It is predicted that although the demand for natural rubber has increased because of the oil shortage, its world-wide production will decrease and that of synthetic rubber will continue to increase. New sources for rubber (guayele and coal) are also being explored. As new types of synthetic rubbers are developed, their use in industries continues to expand (e.g., in the tire, aerospace, automotive and chemical industries, in medicine, metallurgy and electrical engineering). The types of rubbers discussed include butadiene, isoprene, butyl and ethylene-propyl rubbers, nitrile and chloroprene resins, fluorine-containing resins, urethane elastomers and resins with a siloxane-rubber base. References 11: 5 Russian, 6 Western.
[104-9307]

UDC 678.7:678.062:678.065

UTILIZATION OF SYNTHETIC RUBBERS IN TIRE INDUSTRY

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D.I. MENDELEYEVA in Russian Vol 26, No 3, May-Jun 81 pp 247-252

YEVSTRATOV, V. F., corresponding member of USSR Academy of Sciences, laboratory head, Scientific Research Institute of the Tire Industry

[Abstract] A brief history of and recent developments in the use of synthetic rubbers, particularly in the tire industry, are presented. The USSR tire industry uses more than 50% of all rubber produced. Since more than 70% of all manufactured vehicles are trucks, tires for heavy-duty trucks are emphasized by this industry. Poor road conditions and the broad temperature range (from -45 to 55°C) must be considered in tire design. Recent advances have included new designs (e.g., radial tires), which are based on analysis of stress, deformation and wear, new rubber formulations and new fabrication processes (e.g., replacement of gluing tire parts by pressing, automated assembly lines, liquid casting). Research on strengthening elastomers by filling them with industrial carbon, which acts as a heterogeneous catalyst and affects all chemical reactions occurring during processing of rubber mixtures, vulcanization and actual use, has been highly productive. The chemical modification of rubbers by introducing

monofunctional or bi- and polyfunctional compounds into the rubber mixture has also improved rubber quality. Modifiers based on dihydric phenols and some resins have been used extensively in the Soviet tire industry, but there is a wide variety of new chemical modifiers (e.g., mixture of 2,4- and 2,6-toluylenediisocyanates cross-linked with epsilon-caprolactam, metaphenylbismaleimide). These modifiers improve strength, elasticity and fatigue characteristics and adhesion of rubber. Chemical modification of elastomers is regarded as a very promising new field. Figures 2; references 14 (Russian).
[104-9307]

UDC 62.001.6:678.4.013

TECHNICAL PROGRESS IN SYNTHETIC RUBBER INDUSTRY

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D.I. MENDELEYEVA in Russian Vol 26, No 3, May-Jun 81 pp 259-261

KOROTKEVICH, B. S., candidate of technical sciences, State Planning and Scientific Research Institute for the Synthetic Rubber Industry

[Abstract] The history of synthetic rubbers (SRs) is reviewed. Milestones have been the use of metal potassium and lithium catalysts to produce more cold-resistant and elastic rubbers, development of oil- and gas-resistant rubbers, use of synthetic rather than plant-derived ethyl alcohol for SR synthesis, dehydration of butane, use of emulsion polymerization and stereospecific polymerization of isoprene. The increasing replacement of natural rubber by SRs has been facilitated by the production of high-purity monomers (99.9%) and by new highly productive and efficient equipment. More recent developments have been the production of gel-free isoprene rubbers, modified isoprene rubbers with high cohesive strength and one-stage oxidative dehydration of butane. Problems to be solved are the reduction of energy use during monomer production, greater variety of SRs and the modernization of existing facilities. References 5 (Russian).
[104-9307]

UDC 338:678.4.013

ECONOMICS OF SYNTHETIC RUBBER INDUSTRY

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D.I. MENDELEYEVA in Russian Vol 26, No 3, May-Jun 81 pp 262-265

NIKANDROV, A. P., candidate of economic sciences, laboratory head, Technical and Economic Research, State Planning and Scientific Research Institute for the Synthetic Rubber Industry

[Abstract] The synthetic rubber (SR) industry, which holds second place in world-wide SR production, is a major branch of the petrochemical industry and to a great extent determines technical progress and the performance of the economy. Changes in the industry since 1960 have included the replacement of natural by synthetic rubber, the predominant production of isoprene rubber, the decrease in butadiene SR production, a slight decrease in special-purpose rubber production and relocation of production facilities close to sources of raw materials (e.g., western Siberia). Basic factors affecting SR production are net cost, relative capital requirements and labor costs. These factors can be reduced by improvements in technology and production efficiency (e.g., more efficient machinery, increased automation and automatic control systems, efficient organization of maintenance and repair and greater centralization of production, transport and storage facilities). The technology and processes of monomer production, which together with preparation of raw materials is the most costly stage in SR production, should also be improved. The use of synthetic rather than plant-derived ethyl alcohol, for example, has saved 4 million tons of grain and 10 million tons of potatoes annually. The direct use of hydrocarbon raw materials and other new processes (e.g., one-stage dehydration of butane) have reduced net cost by almost 60%. Increasing unit output capacity is also a cost-reducing factor: over the last 20 years average output of the industry has increased 3.3-fold. Environmental protection and efficient use of natural resources are also discussed. Goals for the eleventh Five-Year Plan are greater production of stereoregular rubbers, increase in the production and variety of special-purpose rubbers and acceleration of the growth rate and technical progress of monomer production. References 6 (Russian).
[104-9307]

UDC 541.64:547.315

QUANTUM-CHEMICAL ANALYSIS OF STRUCTURE OF ACTIVE SITES AND POLYMERIZATION MECHANISM OF 1,3-DIENES WITH USE OF ORGANOLITHIUM COMPOUNDS (WITH 1,3-BUTADIENE AS EXAMPLE)

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D.I. MENDELEYEVA in Russian Vol 26, No 3, May-Jun 81 pp 266-272

YERUSALIMSKIY, G. B., junior scientist and KORMER, V. A., professor, doctor of chemical sciences, deputy director for scientific work, All-Union Scientific Research Institute of Synthetic Rubber im. S. V. Lebedev

[Abstract] Quantum-chemical calculations of models of the active sites (AS) of the anionic polymerization of 1,3-butadiene with the use of lithium alkyls in the presence and absence of electron donors were carried out by computer using a modified complete-neglect-of-differential-overlap method. Prereaction complexes of two- and three-component systems such as AS·diene, $(AS)_2$·diene and AS·diene·electron donor were also determined. Aggregates of lithium alkyl derivatives underwent major transformations in the presence of electron donors. These results combined with experimental data yield information on the mechanism of bond formation in polybutadienes as a function of synthesis conditions. Figures 3; references 48: 20 Russian, 28 Western.
[104-9307]

UDC 678.01

PHASE-AGGREGATE STATE OF ELASTOMERS OF VARIOUS STRUCTURES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D.I. MENDELEYEVA in Russian Vol 26, No 3, May-Jun 81 pp 281-288

MAREY, A. I., deceased, KURLYAND, S. K., laboratory head, SIDOROVICH, Ye. A., senior scientist and NOVIKOVA, G. Ye., senior scientist, All-Union Scientific Research Institute of Synthetic Rubber im. S. V. Lebedev

[Abstract] Analysis of the aggregate and phase states of polymers, i.e., their ability to exist as a single aggregate but in different phase states, is vital for solving problems related to the synthesis of polymers with specific physical, mechanical and technical properties. The state of the art of research on the effect of molecular structure on polymer phase-aggregate states and of phase-aggregate states on elastomer mechanical properties is analyzed. Considerable experimental data are cited on the effects of stereoregularity, branching, type and number of substituents, molecular weight, molecular-weight distribution and composition nonuniformity on the phase-aggregate state of basic elastomers and atactic, alternating and block copolymers. Specific data are presented on crystallization kinetic parameters for major elastomers. The degree of

crystallization of elastomers, defects ir and morphology of crystal structure and the state of the amorphous polymer matrix are discussed as the critical mechanical parameters. References 109: 1 Polish, 83 Russian, 25 Western.
[104-9307]

UDC 678.84.074

NEW SILICONE ELASTOMERS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D.I. MENDELEYEVA in Russian Vol 26, No 3, May-Jun 81 pp 297-302

YUZHELEVSKIY, Yu. A., doctor of chemical sciences, sector head and MILESHKEVICH, V. P., laboratory head, All-Union Scientific Research Institute of Synthetic Rubber im. S. V. Lebedev

[Abstract] The production and variety of siloxane rubbers has increased, as well as their application in the aerospace, electrical engineering and radio-electronics industries, medicine and automotive and light industries. Data are reviewed on the synthesis, structure and properties (elasticity, gas and oil resistance, incombustibility) of new silicone elastomers. Methods of siloxane rubber synthesis discussed include polymerization (anionic and homopolymerization), homo- and heterofunctional polycondensation, condensation of chlorosilanes or siloxanes with alkoxy derivatives and polyaddition. Also reviewed is literature on the effect of siloxane chemical structure on product performance. Elastomers discussed include polydimethylsiloxane, carborane siloxane elastomers, gas- and oil-resistant elastomers, siloxane polyblock copolymers with an $(AB)_n$ structure, organodisiloxane copolymers and silicone-polymer-based materials. References 99: 45 Russian, 54 Western.
[104-9307]

UDC 547.1.116.04

REACTIVITY OF MONOMERS USED TO SYNTHESIZE FLUORINE RUBBERS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D. I. MENDELEYEVA in Russian Vol 26, No 3, May-Jun 81 pp 303-310

SOKOLOV, S. V., doctor of chemical sciences and SASS, V. P., candidate of chemical sciences, senior scientist, All-Union Scientific Research Institute of Synthetic Rubber im. S. V. Lebedev

[Abstract] Methods for analyzing the reactivity of monomers that undergo radical polymerization are reviewed. Analysis of the activity of fluorine-containing monomers in model reactions with simple alkyl radicals is preferable to the

determination of the copolymerization constant (relative activity). The use of copolymerization constants is problematic because analysis of monomer behavior during polymerization produces inaccurate data owing to inadequate purification and chemical analysis of individual copolymers; copolymerization constants are also inaccurate owing to the heterogeneity of polymerization of fluorine-containing monomers and vary considerably with polymerization technique. The new method based on model addition reactions is suitable for quantification of monomer activity during copolymerization; the radicals required for kinetic studies are generated by the thermal decomposition of diacyl peroxides in hydrocarbon solutions. The relative rate constants obtained by this method may be used for the same purposes as copolymerization constants, but they are more accurate and experimentally simpler to obtain. The new method will make it possible to determine the participation of new monomers (with the use of small quantities) in copolymerization and to select the optimal reactants, and, as more information is obtained on experimental conditions, solvents, etc., the ability of olefins and other unsaturated compounds to participate in radical reactions will be described by a single quantitative factor. Extensive theoretical and experimental data are presented on reaction energetics and stereochemistry. Tables are included on reaction rate constants for addition of radicals to fluorinated ethylenes and to ethylene and tetrafluoroethylene, for addition of methyl radicals to unsaturated fluorinated hydrocarbons, and for addition of perfluoroalkyl radicals. Figures 1; references 48: 20 Russian, 28 Western.
[104-9307]

UDC 678.664.074:539.389

RELAXATION PROCESSES IN URETHANE ELASTOMERS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D.I. MENDELEYEVA in Russian Vol 26, No 3, May-Jun 81 pp 310-318

SOTNIKOVA, E. N., senior scientist and \PUKHTINA, N. P., doctor of chemical sciences, All-Union Scientific Research Institute of Synthetic Rubber im. S. V. Lebedev

[Abstract] Relaxation processes in multiphase urethane elastomers (milled, molded and thermoplastic polyurethanes) occurring under various structural conditions are discussed. Factors analyzed include elastomer crystallization and glass-transition temperature, molecular weight and proportion of pliable and rigid segments, stress relaxation and its activation energy, viscosity, hysteresis, creep and strength. The structure of the rigid segment in polyurethanes is the major factor in deformation resistance at high temperatures. Figures 6; references 56: 15 Russian, 41 Western.
[104-9307]

UDC 678.023:532.78

EFFECTS OF PULVERIZED VULCANIZED RUBBER ON CRYSTALLIZATION OF CIS-BUTADIENE RUBBERS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNOLOGIYA in Russian Vol 24, No 7, Jul 81 (manuscript received 28 Dec 79) pp 900-903

KOSTRYKINA, G. I., SOLOV'YEV, M. Ye. and ZAKHAROV, N. D., Chair of Chemistry and Technology of Elastomer Processing, Yaroslavl' Polytechnical Institute

[Abstract] Studies were conducted on the characteristics of low temperature (218°K) crystallization of cis-butadiene rubbers containing different amounts of pulverized, analogous, vulcanized rubber. The resultant dilatometric and recovery coefficient data showed that addition of the powder (50-250 μm particles) up to 20% increased the extent and rate of crystallization largely due to a decrease in the density of the matrix. Furthermore, accelerated crystallization during deformation may have also been due to diminished crosslinking and a moderate increase in polysulfide bonds. Increasing the content of the pulverized rubber to 40-50% decreased the extent, rate, and induction period of crystallization, apparently due to an increase in interphase surfaces which reduced the quantity of material capable of crystallization. Figures 3; references 13: 2 Western, 11 Russian.
[144-12172]

SYNTHETIC RUBBER AND RESIN INDUSTRY DURING 11th FIVE-YEAR PLAN

Moscow KAUCHUK I REZINA in Russian No 2, Feb 81 pp 3-4

NEYYENKIRKHEN, Yu. N., USSR Ministry of the Petrochemical Industry

[Abstract] A number of goals was articulated in the "Basic Directives of Economic and Socialist Development in the USSR from 1981 to 1985 and in the period to 1990." Renovation of existing and construction of new plants must incorporate the most progressive technological systems, the most advanced automation and mechanization of processes, and the most efficient methods of operation. Attention must be paid to accelerating technical progress and improving the quality and variety of goods produced. Stereospecific resins, especially of the more complicated compounds, will play an increasingly important role. An example is improving the macrostructure of the SKI-3-01 and SKI-3 resins. In the manufacture of tires, the goals are to develop harder rubbers, to phase in computers to control both the quality of the rubber mixtures and the automatic transfer lines for building and vulcanizing the casings, and to produce a greater variety of better and longer-wearing tires.
[72-12027]

UDC 678.762.2:678.4.045.2

INFLUENCE OF ISOMERIZATION OF CIS-1,4-POLYBUTADIENE UNDER ACTION OF VULCANIZATION-ACCELERATOR ON STRENGTH PROPERTIES OF RESINS

Moscow KAUCHUK I REZINA in Russian No 2, Feb 81
(manuscript received 15 Sep 80) pp 14-17

MARYEY, A. I., deceased, PETROVA, G. P., BERKOVICH, M. A. and VOLKOV, V. P., All-Union Scientific Studies Institute for Synthetic Resins imeni S. V. Lebedev

[Abstract] The title study was conducted using sulfur and other basic accelerators, such as the substituted benzothiazols (al'taksa, kaptaksa, and santokyura) and diphenylguanidines (DPG). The rate and extent of the isomerization reaction increases with the increasing purity of the original rubber, with the series santokyur < kaptaksa < al'taksa < DPG (no isomerization noted), and with increasing concentration of accelerator in the mixture. The reaction kinetics is close to first order. The maximum concentration of the trans isomer was observed in a mixture of SKD-3 with 2 mass parts of al'taksa. The introduction of the vulcanization-activators stearic acid and zinc oxide decreased but did not completely suppress the isomerizing effect of the accelerator. The melting temperatures of the rubber-accelerator mixtures with the activators correlated with both those of similar mixtures without the activators and those of the disaggregated vulcanizing agents. The strength indicators of the vulcanized rubbers decreased with an increase in the isomerizing activity of the accelerator. Figures 2; references 3 (Russian).
[72-12027]

UDC 678.4.023.32

OUTLOOK FOR APPLICATION OF POWDER TECHNOLOGY OF MANUFACTURING RESIN MIXTURES (REVIEW)

Moscow KAUCHUK I REZINA in Russian No 2, Feb 81
(manuscript received 25 Apr 80) pp 30-40

ZAKHARKIN, O. A., ZAKHAROV, N. D. and NEYYENKIRKHEN, Yu. N., Yaroslavl' Polytechnic Institute

[Abstract] A survey of recently published information on the title topic suggests that powder technology may hold the key to organizing a transfer-line manufacturing process for the discrete steps involved in the preparation of mixtures, formation of the intermediate products, and in some cases, also the vulcanization. Powder technology, in addition, permits the preparation of high quality goods based on very viscous resins. Many foreign firms use this technique and under the conditions of the rapidly developing rubber industry

in the USSR, such methods may greatly reduce the necessary capital investment and energy expenditure in the manufacturing plants. Different variations of the basic procedures may be introduced either into existing plants to increase their productivity or incorporated into the design of new plants.
References 89: 39 Russian, 50 Western.
[72-12027]

UDC 66.064-944:541.137

EFFECT OF ALTERNATING CURRENT ON REVERSE OSMOSIS MEMBRANE SELECTIVITY

Moscow TEORETICHESKIYE OSNOVY KHIMICHESKOY TEKHNOLOGII in Russian Vol 15, No 3, May-Jun 81 (manuscript received 6 Apr 79) pp 349-354

DYTNERSKIY, Yu. I., SAVKIN, A. Ye., SOBOLEV, V. D. and CHURAYEV, N. V., Moscow Chemical-Technological Institute imeni D. I. Mendeleyev

[Abstract] Reverse osmosis has been used for separation of liquid mixtures. One of the ways to influence the performance of reverse osmosis membranes is based on the application of an electric field. The mechanism of this phenomenon was studied applying alternate electric current with varying frequency on glass and acetate-cellulose membranes. The experiments showed that the external electric field had no effect on the membrane selectivity toward saccharose. At high frequencies there is no effect on the separation of electrolytic solutions, but at low frequencies the selectivity of both the acetate cellulose and the glass membranes toward the electrolyte solutions is lowered. This observation makes it possible to control the separation processes of the electrolyte mixtures. With current passage, the breakdown of the membranes is accelerated. Therefore, the optimal conditions recommended for the control of membrane selectivity consist of the frequency range ω = from 5 to 10 Hz and the current i = from 5 to $10 \times 10^{-4} A/cm^2$, when the selectivity drops about two-fold, but the membrane breakdown is not as yet too rapid. Figures 5; references 10: 5 Russian, 5 Western.
[110-7813]

UDC 621.593.001.24

INVESTIGATING SINGLE STAGE PROCESS FOR SEPARATING GASEOUS MIXTURE BY MEANS OF ASYMMETRIC MEMBRANE

Moscow TEORETICHESKIYE OSNOVY KHIMICHESKOY TEKHNOLOGII in Russian Vol 15, No 3, May-Jun 81 (manuscript received 28 Apr 80) pp 355-360

CHEKALOV, L. N., TALAKIN, O. G. and NARINSKIY, A. G., Scientific Research Association of Cryogenic Machine Construction

[Abstract] Theoretical calculations for the separation of gaseous mixtures by a single stage membrane process are based on ideal flow conditions of the gases. The calculation is then simple and sufficiently accurate for the first degree of approximation, but with the mixing of the original gas stream, the effectiveness of the process is lowered. Therefore, in the present work, models of ideal expulsion were examined. Equations were derived for the calculation of gas concentration profiles in the perpendicular direction toward the membrane. Selection between models of cross and parallel structures of gas stream was complicated because, in the zone of low pressures, currents exist both parallel and perpendicular to the membrane. Calculations based on the gas flow parallel to a polyvinyltrimethylsilane membrane were found to agree well with experimental data. Figures 3; references 6: 4 Russian, 2 Western.
[110-7813]

UDC 552.5:005

CHARACTERISTICS OF OIL SHALES

Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 30, No 1, Jan-Mar 81 (manuscript received 1 Apr 80) pp 1-4

VESKI, R., Institute of Chemistry, ESSR Academy of Sciences

[Abstract] The term "oil shale" or, literally, "combustible shale", has been ascribed to a divergent group of highly organic rocks. The term is now restricted to rocks containing 10-50% organic matter which was deposited at the same time as the inorganic fraction of the rock. The organic matter type covers the entire range from sapropelic (algal) to humic (terrestrial). The rank of the organic material is immature, corresponding to that of "rock-coal" or lower, and thus the organic material is virtually insoluble in low-boiling organic solvents. Oil shales are distinguished from coals (organic matter > 50%) and from normal shales (organic matter < 10%). Other classifications have been proposed based on such parameters as combustibility, oil yield, etc., but are not universally applicable. Figures 2; references 29: 27 Russian, 2 Western.
[75-12027]

UDC 66.048+662.756

DETERMINATION OF FRACTIONAL COMPOSITION OF SHALE OIL USING SIMULATED DISTILLATION

Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 30, No 1, Jan-Mar 81 (manuscript received 27 May 80) pp 5-9

SALUSTE, SAYMA, LUYK, Kh. and KLESMENT, I., Institute of Chemistry, ESSR Academy of Sciences

[Abstract] The boiling point ranges of several shale oils were determined using a short (1.5m) OV-101 packed column and standard chromatograph. Temperature calibration was carried out at several programming rates using normal paraffins.

Data are presented in both differential (standard chromatographic) and integral (cumulative)forms. The yield (Y) can be calculated from the equation

$$Y = (100xK_s xE_s)/K_y E_y$$

where E_s and E_y are the peak heights of the standard and the sample respectively and K_s and K_y are the specific gravities of the standard and the sample respectively. Analytical error is in the range of 5%. This technique can be applied to samples with specific gravities as high as 0.960 g/cm^3, characteristic of oils with the heaviest fractions boiling at about 400°C. Figures 2; references 7: 2 Russian, 5 Western.
[75-12027]

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